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(54) **Catalytically active gas diffusion electrodes comprising a nonwoven fibrous structure**

(57) The object of the present invention is to provide a gas diffusion electrode with both increased dimensional stability and flexibility and which can therefore be produced at lower cost. A further object is to provide an improved manufacturing process that is capable of producing large numbers of electrodes and MEAs at low unit cost, in high volumes and with high yields.

Accordingly, there is provided a gas diffusion electrode comprising a non-woven network of fibres, one or more catalyst components and at least one polymeric substance characterised in that the catalyst component is embedded within the fibre network. Generally, the non-woven network of fibres has a density of less than 0.3 g/cm³, suitably less than 0.2 g/cm³ and preferably less than 0.1 g/cm³.

Fibres which are suitable for use in the present invention include carbon, glass, polymer, metal or ceramic fibres, preferably carbon, glass, metal or ceramic, typically of diameters in the range of 0.2µm to 50µm and with lengths from 0.05mm to 300mm, suitably 0.5mm to 150mm. If fibres other than carbon fibres or other elec-

trically conducting fibres are used it is necessary that the catalyst component comprises carbon and optionally one or more other catalyst components such as metal or a metal supported on carbon in order that the final electrode structure is electrically conducting.

The polymeric substances act as a binder to hold the electrode layer together. Depending on the polymeric substance used it may also act to provide essential electrode structural properties, such as control of the hydrophobic/hydrophilic balance. Examples of such polymers include polytetrafluoroethylene (PTFE), fluorinated ethylene-propylene (FEP), polyethylene, polypropylene, ethylene-propylene. The polymeric material can also act to provide the ionic conduction pathway in the electrode. Such proton conducting polymers are for example the perfluorosulphonic acid materials, produced by E.I. DuPont de Nemours, referred to as Nafion®.

The gas diffusion electrodes of the present invention are of use in electrochemical devices, including metal-air batteries, electrochemical gas sensors, and in electrosynthesis, and, particularly in fuel cells.

the catalyst layer. Additionally it also enables a mechanically stable gas diffusion electrode to be produced.

A major problem with conventional gas diffusion electrodes based on the carbon fibre paper substrates is the lack of flexibility due to the rigid substrate that is typically used. The conventional electrodes are consequently easily damaged on handling which leads to high reject rates during the electrode and MEA fabrication process. This obviously has an impact on cost. With conventional gas diffusion electrodes based on woven cloth substrates a problem concerns the lack of good dimensional stability, as the cloth can easily be stretched in the directions of the major planar faces (x and y directions). This can make the manufacturing of electrodes and MEAs using these substrates very difficult and therefore costly.

Furthermore the complexity of the conventional gas diffusion electrode requires a number of separate components such as the substrate and the catalyst layers to be brought together which results in a lengthy manufacturing process requiring a number of steps. Again, this increases the cost per unit of these gas diffusion electrodes to higher than is currently acceptable to make applications in power generation devices, such as fuel cells, commercially viable.

It is therefore an object of the present invention to provide a gas diffusion electrode with both increased dimensional stability and flexibility and which can therefore be produced at lower cost. A further object of the present invention is to provide an improved manufacturing process that is capable of producing large numbers of electrodes and MEAs at low unit cost, in high volumes and with high yields.

Accordingly, the present invention provides a gas diffusion electrode comprising a non-woven network of fibres, one or more catalyst components and at least one polymeric substance characterised in that the catalyst component is embedded within the fibre network. Generally, the non-woven network of fibres has a density of less than 0.3 g/cm³, suitably less than 0.2 g/cm³ and preferably less than 0.1 g/cm³.

The fibres, within the matrix, are normally randomly orientated in the x and y direction (in-plane) producing a two dimensional isotropic structure. Additionally, random orientation in the z direction (through-plane) occurs with the inclusion of very short fibres, typically lengths of ≤ 2mm or very fine fibres, typically of diameters ≤ 1 µm. It is also possible to introduce anisotropic character into the fibre matrix by using longer fibres, typically ≥ 50mm, in the composition, in combination with any method of laying down the layer that imparts a directional force into the mixture, such as extrusion or a paper making type processes. Fibres which are suitable for use in the present invention include carbon, glass, polymer, metal or ceramic fibres, preferably carbon, glass, metal or ceramic, typically of diameters in the range of 0.2µm to 50µm and with lengths from 0.05mm to 300mm, suitably 0.5mm to 150mm if fibres other than

carbon fibres or other electrically conducting fibres are used it is necessary that the catalyst component comprises carbon and optionally one or more other catalyst components such as a metal or a metal supported on carbon in order that the final electrode structure is electrically conducting.

By the term catalyst is meant a material that promotes or enhances the rate of the reaction of interest but remains unaltered by the reaction. The catalyst component or components selected will depend on the application for which the gas diffusion electrode is being used. These may be, for example, a precious metal or a transition metal as the metal or metal oxide, either unsupported or supported in a dispersed form on a carbon support; a carbon or an organic complex, in the form of a high surface area finely divided powder or fibre, or a combination of these options.

The polymeric substances act as a binder to hold the electrode layer together. Depending on the polymeric substance used it may also act to provide essential electrode structural properties, such as control of the hydrophobic/hydrophilic balance. Examples of such polymers include polytetrafluoroethylene (PTFE), fluorinated ethylene-propylene (FEP), polyethylene, polypropylene, ethylene-propylene. The polymeric material can also act to provide the ionic conduction pathway in the electrode. Such proton conducting polymers are for example the perfluorosulphonic acid materials, produced by E.I. DuPont de Nemours, referred to as Nafion®.

A first embodiment of the present invention provides a gas diffusion electrode as hereinbefore described wherein the catalyst component is one or more metals or their oxides in the form of finely divided unsupported powders or as metals in a dispersed form on a carbon support. Suitably the one or more metals may be a precious metal (Pt, Pd, Ru, Rh, Ir, Os, Au and Ag) or a transition metal selected from groups IVB, VB, VIB, VIIIB, VIII, IB or IIB of the Periodic Table in "Handbook of Chemistry and Physics", 64th Edition, CRC Press, or a combination or alloy thereof. Preferably, the one or more metals is a precious metal, particularly Pt, or an alloy thereof.

A second embodiment of the invention provides a gas diffusion electrode as hereinbefore described wherein the catalyst component is one or more carbon blacks.

A major advantage of the present invention is that a free-standing, dimensionally stable and highly flexible gas diffusion electrode is obtained. The incidence of damage to the electrode on handling during manufacture is therefore minimised thus reducing the number of faulty or rejected electrodes, and consequently the cost is reduced. Furthermore, the intrinsic material cost is significantly reduced over carbon paper or woven cloths. In addition, the electrode of the invention is more amenable to high volume continuous production processes due to its high dimensional stability.

A further advantage of the gas diffusion electrodes

losses occur in cells operating with hydrogen as the fuel. The MEAs were fabricated by hot pressing the anode and cathode against each face of the solid proton conducting electrolyte membrane, as is commonly practised in the art.

The anodes were of the more conventional type, currently widely employed in the PEMFC. They comprised a conventional pre-tفلonated rigid conducting carbon fibre paper substrate (Toray TGP-H-090, available from Toray Industries Inc, Tokyo, Japan) to which was applied a layer of a 20 wt% platinum, 10 wt% ruthenium catalyst, supported on Cabot Vulcan XC72R (from Johnson Matthey Inc, New Jersey, USA), at an electrode platinum loading of 0.25 mg/cm² of electrode geometric area. The MEAs were evaluated in a PEMFC single cell, with a geometric electrochemically active area of 50 cm². The single cell consisted of graphite plates into which flowfields were machined to distribute reactant gases and humidification water, and remove products. The MEA was located between the flowfield plates. The operation of the single cell was controlled from a purpose built test station facility (from GlobeTech, of Bryan, Texas, USA). The "performance" of the fuel cell was assessed by measuring the voltage and current density relationship using a standard operating procedure. Unless otherwise stated, these conditions were typically, a reactant gas inlet temperature of 80°C, a pressure of both anode and cathode reactant gases of 3 atmospheres, and a reactant stoichiometry of 1.5 for hydrogen and 2.0 for air.

EXAMPLE 1

A first particulate catalyst component was provided by dispersing 50 weight parts of a carbon black (Shawinigan black, from Chevron Chemicals, Houston, Texas, USA) in 1200 parts of demineralised water. To this was added 6 weight parts of polytetrafluoroethylene (PTFE) as a dispersion in water (ICI Fluon GP1, 64 wt% solids suspension) and the mixture stirred to entrain the PTFE particles within the carbon catalyst material. The slurry was redispersed using a high shear mixer to produce a smooth mixture.

A second particulate catalyst material was provided by dispersing 100 weight parts of a 40 wt% platinum catalyst, supported on carbon black (Johnson Matthey FC-40) in 30 parts of a 9.5% dispersion of Nafion EW1100 (E I DuPont De Nemours & Co.) in water, prepared according to methods described in EPA 731,520. The particulate catalyst was dispersed using a high shear mixer to produce a smooth mixture.

A pre-formed non-woven carbon fibre structure was a 17g/m² (\approx 0.07g/cm²) density carbon fibre mat, supplied as Optimat 203 (from Technical Fibre Products, Kendal, Cumbria, UK). This was precoated with PTFE by soaking for 5 minutes in a solution of 120 parts by weight of GP1 PTFE emulsion in 2100 parts by weight of water then draining and allowing to dry. The coated

carbon fibre mat was heated to 350°C in air to sinter the PTFE.

The electrode of the invention was formed by pressing the first particulate catalyst material into the non-woven carbon fibre structure using a vacuum bed to remove the water and pull the particulate catalyst material into the structure. A total fill of 11.7g Shawinigan carbon per cm² carbon fibre paper geometric area was achieved. The resulting sheet was pressed at 260°C and 1501b per sq inch for 2 minutes to compact the structure. A layer of the second particulate catalyst material was then applied to one face of the filled non-woven structure to provide a platinum loading of 0.76 mg/cm² geometric area within the remaining carbon fibre structure and pressed at 2001b per square inch to compact the layer.

The electrode formed the cathode of an MEA, with the face of the electrode comprising the platinum catalyst component bonded to the membrane electrolyte face. The membrane employed was Du Pont Nafion 112. The single cell results are shown in Figure 1 and demonstrate that good cell performances were obtained from the MEA comprising the lower cost, more manufacturable electrode of the invention. For operation on pure oxygen very high current densities of over 2.0 A/cm² were obtained. For most practical applications of the PEMFC, the oxidant will be air, and these applications will require that at least a current density of 500 mA/cm² is achieved. As illustrated in the Figure, current densities up to 1.0 A/cm² were obtained, and the results represent performances typical of a satisfactorily performing MEA. It is worth noting that on air operation there was a tendency for the cell voltage to decrease more rapidly as the current density increased toward 1.0 A/cm², compared to the pure oxygen data. This is an example of cell voltage decrease due to mass transport losses, relating to the ease with which reactant oxygen in air can diffuse to the electrode reaction sites. This is also a typical characteristic of cell current vs voltage plots seen with conventional MEAs, fabricated with electrodes comprising conducting substrates such as high density carbon fibre paper.

EXAMPLE 2

A first particulate catalyst material was prepared by dispersing 80 weight parts of Shawinigan carbon black in 1200 parts of water. To this was added 20 weight parts of polytetrafluoroethylene solids (PTFE) as a dispersion in water (ICI Fluon GP1, 64 wt% solids suspension) and the mixture stirred to entrain the PTFE particles within the carbon catalyst material. The slurry was redispersed using a high shear mixer to produce a smooth mixture.

Chopped carbon fibres (Type RK 10, from RK Carbon Fibres Ltd, UK) at a fibre length of 37 mm were treated with GP1 polytetrafluoroethylene dispersion in water to give a 7 wt% coating on the fibres. Further RK10 fibres of length 12mm and 1mm were similarly treated.

6. A gas diffusion electrode according to any preceding claim wherein the catalyst component is one or more metals or their metal oxide, in the form of finely divided unsupported powders or as metals in a dispersed form on a carbon support. 5
7. A gas diffusion electrode according to claim 6 wherein the catalyst component is selected from one or more precious metals or a transition metal or a combination or alloy thereof 10
8. A gas diffusion electrode according to any one of claims 1 to 5 wherein the catalyst component is one or more carbon blacks. 15
9. A method for the manufacture of the gas diffusion electrode according to any preceding claim comprising mixing the fibres with at least one catalyst component or a polymeric substance and thereafter forming the gas diffusion electrode by adapting a continuous manufacturing process. 20
10. A method according to claim 9 wherein the continuous manufacturing process is based on paper-making technology. 25
11. A membrane electrode assembly wherein one or both of the gas diffusion electrodes is an electrode according to any one of claims 1 to 8. 30
12. A fuel cell which comprises a gas diffusion electrode according to any one of claims 1 to 8.

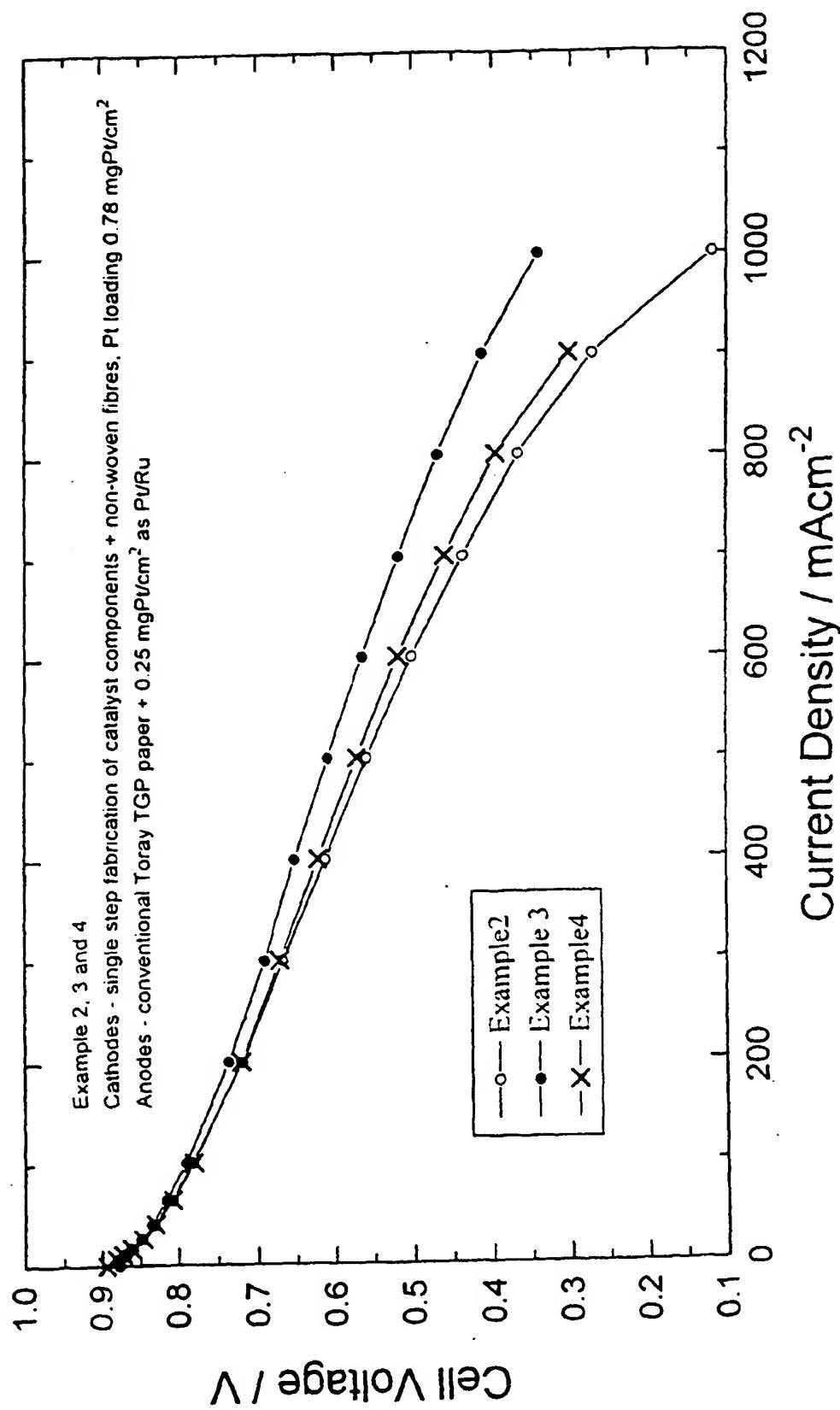
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Figure 2



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EUROPEAN SEARCH REPORT

Application Number
EP 97 30 0921

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	EP 0 654 837 A (JOHNSON MATTHEY PLC) 24 May 1995 * examples 1-3 * ---		
A	US 5 308 465 A (HILLRICH & EILHARD ET AL) 3 May 1994 * column 3, line 19-29 * * figure 1 * -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.)
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
MUNICH	20 May 1997	Engl, H	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non written disclosure P : intermediate document			